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7-Deaza-2′-deoxyisoguanosine adopts the form of an N1—H,2-keto tautomer

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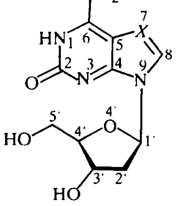
Abstract

The structure of the title hydrate [4-amino-7-(2-deoxy-β-D-*erythro*-pentofuranosyl)-3,7-dihydro-2*H*-pyrrolo[2,3-*d*]pyrimidin-2-one hydrate, $C_{11}H_{14}N_4O_4\cdot H_2O$], an analogue of 2′-deoxyisoguanosine, was determined by single-crystal X-ray diffraction. The glycosylic torsion angle [$\chi = -118.3(3)°$] is in the *anti* conformation range and the sugar ring adopts a C1′-*exo* pucker. The molecule shows the N1—H,2-keto-6-amino tautomeric form in the solid state.

Comment

Parallel-stranded (ps) DNA duplexes formed by oligonucleotides containing isoguanine and/or 5-methylisocytosine have been realised (Seela *et al.*, 1993; Sugiyama *et al.*, 1996; Seela & Wei, 1997*a*). Also, DNA quartets have been constructed from oligodeoxyribonucleotides containing short runs of isoguanine residues (Seela *et al.*, 1996). More recently, the solution structure of a ps-DNA duplex containing isoguanine and 5-methylisocytosine bases has been determined by NMR analysis (Yang *et al.*, 1998). It was demonstrated that the structural characteristics of the refined ps-duplex are different from those of B-DNA and that most of the nucleosides, including 2′-deoxyisoguanosine, are in the *anti* conformation and show a C2′-*endo* pucker. Recently, an isosteric analogue of 2′-deoxyisoguanosine, namely 7-deaza-2′-deoxyisoguanosine, (1) (purine numbering is used throughout the manuscript), has been synthesized and incorporated into oligonucleotides. Similar thermodynamic base-pair stability and selectivity were observed in the case of 7-deaza-2′-deoxyisoguanosine compared to 2′-deoxyisoguanosine (Seela & Wei, 1999).



(1) *X* = CH
(2) *X* = N

Crystal structures related to compound (1) have been reported. They include isoguanine sulfate monohydrate (Subramanian & Marsh, 1971), 9-methylisoguanine hydrochloride dihydrate (Banerjee *et al.*, 1978), 1-methylisoguanine dihydrate (Wong & Nachman, 1984), and 1-allylisoguanosine (Liaw *et al.*, 1992). However, a search of the Cambridge Structural Database revealed that no crystal structures of 7-deazaisoguanine derivatives or of isoguanine 2′-deoxyribonucleosides have been determined. To obtain the conformation of the title compound, (1)·H_2O, its X-ray analysis was performed.

The three-dimensional structure of 7-deaza-2′-deoxyisoguanosine is shown in Fig. 1. Selected bond distances and angles of (1)·H_2O are presented in Table 1. It is apparent that the ring proton is localized at N1 and the molecule adopts the N1—H,2-keto-6-amino tautomeric form (Sepiol *et al.*, 1976). This is in line with the structure of 2′-deoxyisoguanosine, (2), in aqueous solution (Seela *et al.*, 1995). The same tautomeric species of 2′-deoxyisoguanosine has been detected in a crystal structure of a DNA duplex (Robinson *et al.*, 1998). In such an antiparallel duplex, the isoguanine can also adopt an enol form resulting in base pairing with thymine. This shows that the isoguanine can form different tautomeric states much more easily than guanine, which results in mutagenic events (Kamiya & Kasai, 1997).

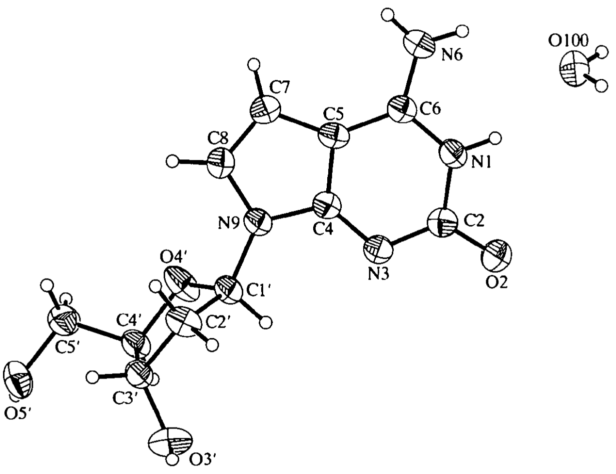


Fig. 1. Perspective view of 7-deaza-2′-deoxyisoguanosine showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are drawn at 50% probability level. H atoms are shown as spheres of an arbitrary size.

The nucleobase of (1) is planar. The deviations of its C and N atoms from the least-squares planes are in the range of ±0.016 Å [N1 = 0.004 (2), C2 = −0.016 (2), N3 = −0.003 (2), C4 = 0.006 (3), C5 = −0.003 (3), C6 = 0.016 (2), C7 = −0.016 (2), C8 = −0.004 (2), N9 = 0.016 (2) Å]. The O2 substituent of (1) lies 0.049 (3) below and the N atom of the 6-amino group 0.034 (4) Å above this plane. The sugar conformation is C1′-*exo* envelope ($_1E$) as it has been observed for 1-allylisoguanosine (Liaw *et al.*, 1992). The glycosylic torsion angle [$\chi = -118.3\,(3)°$] is in the *anti* range (Seela *et al.*, 1999).

Each nucleobase is complexed by one H_2O molecule which is coordinated by hydrogen bonding. The water O atom (O100) acts as a receptor of two hydrogen bonds from the H atom of N1 (H1*A*), and one of the H atoms of the 6-amino group (H6*A*). The position of O100 is located 0.077 (4) Å above the plane of the base. The other intermolecular hydrogen bonds which stabilize the structure are summarized in Table 2. No tetrameric assembly is observed in the crystal structure, while such a structure has been detected in aqueous solution (Seela & Wei, 1997*b*).

Experimental

The nucleoside (1)·H_2O (Seela *et al.*, 1986) was prepared by selective deamination of 2-amino-7-deaza-2′-deoxyadenosine (Seela *et al.*, 1987) with sodium nitrite in aqueous acetic acid at room temperature (Seela & Wei, 1997*b*). After purification by chromatography on a hydrophobic resin column (Serdolit AD-4, 0.1–0.2 mm, Serva, Germany), (1)·H_2O was crystallized from $H_2O/^iPrOH$ (95:5) (Seela & Wei, 1999). For the diffraction experiment a single crystal was fixed at the top of a Lindemann capillary with epoxy resin.

Crystal data

$C_{11}H_{14}N_4O_4{\cdot}H_2O$
$M_r = 284.28$
Orthorhombic
$P2_12_12_1$
$a = 6.8040\,(8)$ Å
$b = 10.0373\,(10)$ Å
$c = 18.682\,(2)$ Å
$V = 1275.9\,(3)$ Å^3
$Z = 4$
$D_x = 1.480$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 4.81$–$13.91°$
$\mu = 0.118$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*SHELXTL*; Sheldrick, 1997*a*)
$T_{\min} = 0.847$, $T_{\max} = 0.977$
2638 measured reflections
2235 independent reflections
1864 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\max} = 25°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.078$
2235 reflections
189 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.0584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.141$ e Å^{-3}
$\Delta\rho_{\min} = -0.181$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C6	1.351 (3)	C8—N9	1.400 (3)
N1—C2	1.398 (3)	N9—C1′	1.448 (3)
C2—O2	1.258 (3)	C1′—O4′	1.428 (3)
C2—N3	1.337 (3)	C1′—C2′	1.519 (4)
N3—C4	1.351 (3)	C2′—C3′	1.517 (4)
C4—N9	1.364 (3)	C3′—O3′	1.426 (4)
C4—C5	1.401 (4)	C3′—C4′	1.531 (4)
C5—C6	1.395 (4)	C4′—O4′	1.442 (3)
C5—C7	1.434 (4)	C4′—C5′	1.514 (4)
C6—N6	1.332 (3)	C5′—O5′	1.429 (4)
C7—C8	1.350 (4)		
C6—N1—C2	125.2 (2)	C8—C7—C5	107.0 (2)
N3—C2—N1	119.8 (2)	C7—C8—N9	109.2 (2)
C2—N3—C4	115.2 (2)	C4—N9—C8	108.8 (2)
N3—C4—N9	124.9 (2)	O4′—C1′—C2′	103.8 (2)
N3—C4—C5	127.5 (2)	C3′—C2′—C1′	102.6 (2)
N9—C4—C5	107.6 (2)	O3′—C3′—C2′	112.6 (2)
C6—C5—C4	116.0 (2)	O3′—C3′—C4′	107.8 (2)
C6—C5—C7	136.7 (2)	C2′—C3′—C4′	103.8 (2)
C4—C5—C7	107.4 (2)	O4′—C4′—C3′	106.9 (2)
N1—C6—C5	116.3 (2)	C1′—O4′—C4′	107.6 (2)

C4—N9—C1′—O4′	−118.3 (3)	C2′—C3′—C4′—O4′	5.7 (3)
C8—N9—C1′—O4′	62.9 (4)	O3′—C3′—C4′—C5′	126.4 (3)
C4—N9—C1′—C2′	125.3 (3)	C2′—C3′—C4′—C5′	−114.0 (3)
C8—N9—C1′—C2′	−53.6 (4)	N9—C1′—O4′—C4′	−160.1 (2)
O4′—C1′—C2′—C3′	38.8 (3)	C2′—C1′—O4′—C4′	−36.3 (3)
N9—C1′—C2′—C3′	158.1 (2)	C5′—C4′—O4′—C1′	142.2 (3)
C1′—C2′—C3′—O3′	89.8 (3)	C3′—C4′—O4′—C1′	19.2 (3)
C1′—C2′—C3′—C4′	−26.5 (3)	O4′—C4′—C5′—O5′	178.3 (2)
O3′—C3′—C4′—O4′	−113.9 (3)	C3′—C4′—C5′—O5′	−62.9 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O100	0.86	2.04	3.044 (3)	144
N6—H6*B*···O3′[i]	0.86	2.06	2.891 (3)	161
O3′—H3′*B*···N3[ii]	0.82	2.01	2.773 (4)	154
O5′—H5′*A*···O2[iii]	0.82	1.90	2.716 (3)	176
O100—H101···O5′[iv]	0.86 (2)	2.05 (3)	2.866 (3)	159 (3)
O100—H102···O2[v]	0.86 (2)	1.99 (2)	2.846 (3)	176 (4)

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, \frac{5}{2}-y, 1-z$; (iii) $x-\frac{1}{2}, \frac{5}{2}-y, 1-z$; (iv) $\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (v) $-x, y-\frac{1}{2}, \frac{3}{2}-z$.

With the absence of suitable anomalous scatterers within the molecule, the determination of the absolute configuration was not possible from our X-ray data. However, comparison with the configuration of the parent molecule indicates that the proposed conformation is correct.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1997*a*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*c*). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1322). Services for accessing these data are described at the back of the journal.

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5,7-Diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine at 122 K

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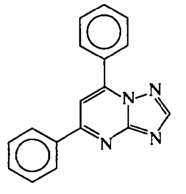
Abstract

The title compound, $C_{17}H_{12}N_4$, belongs to a group of N-bridgehead purine analogue ligands. The nine atoms comprising the triazolopyrimidine core have an r.m.s. deviation of 0.023 Å from the mean plane. The two phenyl groups attached to the core form interplanar angles of 27.38 (6) and 55.76 (3)° with this core plane.

Comment

Many derivatives of bicyclic [*a*]-heteroannulated pyrimidine are known as compounds of interesting coordinating properties for metal ions. Crystal structures have been reported for several metal complexes with ligands of this type (Biagini Cingi *et al.*, 1987, 1983; Haasnoot *et al.*, 1984). Therefore it is surprising that the structures of the free ligands have not been described in the literature (Cambridge Structural Database; Allen *et al.*, 1983). In order to enable the comparison between a free and a coordinated ligand, we undertook the structure determination of 5,7-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine, subsequently referred to as dptp.



dptp

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